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Influence of complex formation on the electronic structure of uranyl[☆]

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Abstract

The spectroscopic properties of uranyl nitrate complexes in aqueous solution are described. Absorption spectra in the range of 20 000–28 000 cm^{-1} are recorded. Three different complexes are formed: $UO_2NO_3^+$, $UO_2(NO_3)_2$ and $UO_2(NO_3)_3^-$. A computer routine was written to calculate the concentrations of the different species in solution. The molar absorptivity of each species at each wavelength is determined. The calculated spectra are compared with literature data. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The uranyl ion (UO_2^{2+}) has a very characteristic absorption spectrum. The spectroscopic properties of the uranyl ion were first investigated by Brewster [1] in the middle of the 19th century and afterwards generations of spectroscopists continued his early work. UO_2^{2+} can easily form complexes with various types of ligands: simple inorganic ligands (e.g. NO_3^-, Cl^-, CO_3^{2-}, SO_4^{2-}), small organic ligands (e.g. CH_3COO^-, $C_2O_4^{2-}$) or macrocyclic ligands (e.g. Schiff bases, crown ethers). Hitherto, the optical properties of uranyl in the solid state (powder form, single crystals) and in melt systems were extensively studied [2–22], but studies concerning the spectroscopic problems in solution are scarce [2–6]. Recently, the study of uranyl complexes in solution regained interest [23–31].

In this paper, we describe the spectroscopic properties of uranyl nitrate complexes in aqueous solution. Three different complexes are formed: $UO_2NO_3^+$, $UO_2(NO_3)_2$ and $UO_2(NO_3)_3^-$ [5]. By means of the stability constants, the concentrations of these three species, as well as the free UO_2^{2+} and NO_3^- concentrations in solution are calculated. As a result, the molar absorptivity of each species at each wavelength is determined. In other words, it is possible to extract the absorption spectrum of each component from that of a mixture of complexes. The calculated spectra are compared with literature data.

2. Theory

A computer routine was written to calculate the concentrations of the different species in solution.

The stepwise formation of a ML_m complex in solution (where M represents a metal ion, L can be any ligand and m is the co-ordination number) can be described by m formation constants K. If L is obtained by the deprotonation of an acid H_nL, the n stability constants, K_z have to be taken into account. Although the routine is written for any general case, we shall exemplify its use by discussing a specific case. Imagine a system where a metal ion M forms three complexes with ligand L, obtained from a monoprotic acid HL. Thus m equals three. The equilibria in this system can be written as (simplified by leaving out the charges):

$$K_1 = \frac{[ML]}{[M]\cdot[L]}; K_2 = \frac{[ML_2]}{[ML]\cdot[L]}; K_3 = \frac{[ML_3]}{[ML_2]\cdot[L]};$$

$$K_z = \frac{[HL]}{[H]\cdot[L]} \tag{1}$$

(Note that K_z is defined as an association constant and not as a dissociation constant as normally used.)

The total metal concentration, C_M and the total ligand concentration, C_L can be expressed as:

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$$C_M = [M] + [ML] + [ML_2] + [ML_3]$$
$$C_L = [L] + [HL] + [ML] + 2 \cdot [ML_2] + 3 \cdot [ML_3] \quad (2)$$

If the equilibrium constants are known, as well as C_M, C_L and the pH, the concentration distribution of all the species, formed in the solution can be calculated. The problem is this of solving a set of determined equations. The routine for solving this set of equations is based on Laguerre's method for finding the roots of polynomials [32]. This method is by far the most straightforward of the general methods used. For each solution prepared, this provides us with a row matrix C of the concentrations c of each species in the solution. For several solutions k of the same chemical system under varying conditions, the matrix C is a $(z \times k)$ matrix, z being the number of species in the solution.

An experimentally observed absorbance a_{ik} at the wavelength i in k solutions, within the validity range of Beer's Law, is a sum of products of molar absorptions ε_{ij} of z species with its concentration c_{jk} in the kth sample according to Eq. (3):

$$a_{ik} = \varepsilon_{i1} \cdot C_{1k} + \varepsilon_{i2} \cdot C_{2k} + \cdots + \varepsilon_{iz} \cdot C_{zk}$$

or

$$a_{ik} = \sum \varepsilon_{ij} \cdot C_{jk} \quad (3)$$

The matrix $A(i \times k)$ of absorbances a_{ik} measured at a range of wavelengths i in k solutions can be expressed by matrix formulation as: $A = E.\ C$, where E is a matrix $(i \times z)$ of the molar absorbances ε of each species at the measured wavelength and C the $(z \times k)$ concentration matrix. The columns of E contain the single component spectra of the relevant species.

We want to find a good estimate for the set of ε_{ij}. The observational model is a general linear model, because the dependent variable a_{ik} is described as a function of several independent variables c_{jk}. The column matrix $\hat{E}$ represents the matrix of the least-squares estimates for the absorptivities of this linear model. This matrix can be calculated as follows:

$$\hat{E} = (C^T \cdot C)^{-1} \cdot C^T \cdot A$$

where C^T is the transpose of C. The matrix solution gives the set of $\hat{\varepsilon}_{ij}$ in the linear model that minimises

$$\sum_i (a_{ik} - \hat{a}_{ik})^2$$

for the data collected.

The written routine for this part of the calculation is based on Singular Value Decomposition (SVD) [32]. In the case of an overdetermined system (more experimental data than unknowns or $k > z$), SVD produces a solution that is the best approximation in the least-squares sense. The overdetermined linear problem is reduced to a solvable linear problem.

3. Experimental details

$UO_2(ClO_4)_2 \cdot 6H_2O$ was prepared according to the method of Silverman and Moudy [33]: UO_3 was dissolved in perchloric acid (2 M). The solution was boiled to expel free chlorine. After dilution with water, the solution was subsequently evaporated till almost dry. This procedure was repeated until there were no longer white fumes. A yellow powder is obtained. The purity of the uranyl perchlorate complex was determined by a gravimetric analysis with 8-hydroxyquinoline.

The solutions were prepared in aqueous medium from a standard solution of UO_2^{2+} (ca. 2×10^{-2} M) with gradually raised concentrations of nitric acid ranging from 0.1 to 1.0 M. The ionic strength was adjusted to 1.0 M by addition of $NaClO_4$. Additional solutions were prepared with higher concentrations of nitric acid.

The absorption spectra of $UO_2(NO_3)_2 \cdot 6H_2O$ and $CsUO_2(NO_3)_3$ were obtained from a homogeneous mixture of the powder of the complex and silicon grease.

Absorption spectra were recorded at room temperature in the range of 20 000–28 000 cm^{-1} using an AVIV 17 DS spectrophotometer.

The routines to analyse the experimental data, resulting in single component spectra are written by the authors and based on classical numerical recipes [32].

4. Results and discussion

The theory is illustrated by the complexation of UO_2^{2+} with NO_3^- ligands in aqueous solutions. The formation of three different complexes is observed: $UO_2NO_3^+$, $UO_2(NO_3)_2$ and $UO_2(NO_3)_3^-$. This system can be characterised by three formation constants: $K_1 = 0.5$ [34,35], $K_2 = 1.0$ [35] and $K_3 = 0.9$ [35]. K_1 and K_2 were determined in $NaClO_4$ medium at ionic strength of 1.0; K_3 in media of varying HNO_3 concentrations. A wide range of values for K_2 and only a few for K_3 can be found in the literature and none of the authors are in agreement [35]. The physical meaning of the increasing values of the constants is not clear (one would expect $K_1 > K_2 > K_3$).

Nitric acid is a strong acid and is therefore completely dissociated. The association constant K_z can be set equal to zero and the pH must not be taken into account.

The distribution of the different species in the solution is illustrated in terms of α-values in Fig. 1.

The absorbance matrix A is constructed from UV–Vis spectra in the range of 20 000–28 000 cm^{-1} of 42 samples. An example of the absorption spectrum of a number of the prepared solutions is shown in Fig. 2. The total metal and ligand concentration, C_M and C_L are added in the legend. Table 1 gives the calculated concentration of

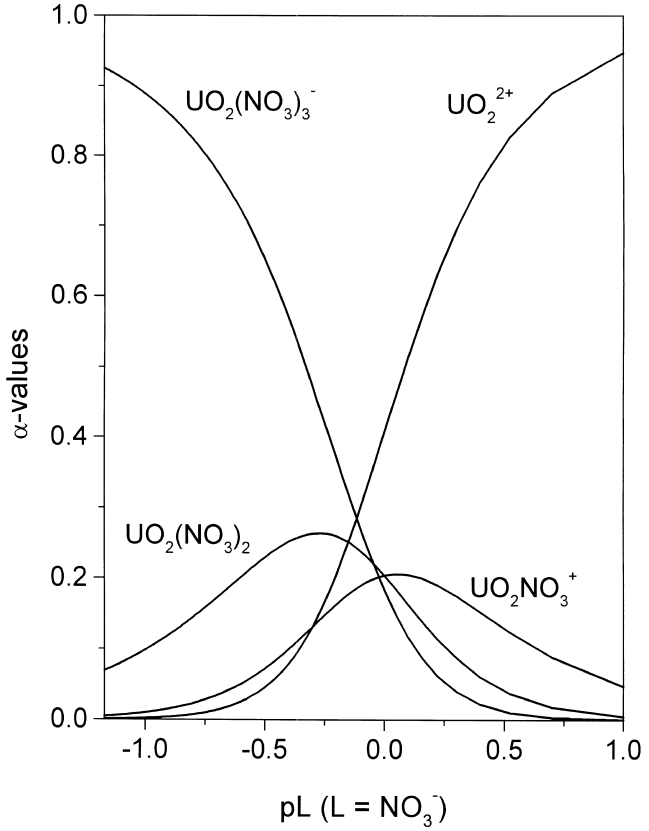

Fig. 1. α-values for the distribution of the different species as a function of the ligand concentration. $C_M = 2\times10^{-2}$ M; C_L ranges from 0.1 to 15 M.

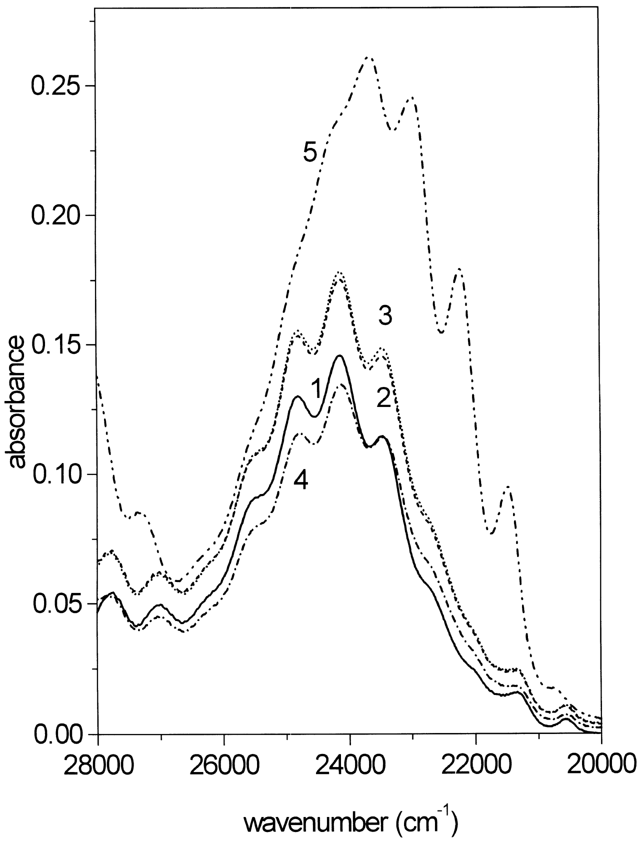

Fig. 2. UV–Vis spectra of five samples with varying concentrations of UO_2^{2+} and NO_3^-. (1) $C_M = 2.07\times10^{-2}$ M; $C_L = 2.47\times10^{-1}$ M; (2) $C_M = 2.35\times10^{-2}$ M; $C_L = 1.07$ M; (3) $C_M = 1.86\times10^{-2}$ M; $C_L = 1.14$ M; (4) $C_M = 1.76\times10^{-2}$ M; $C_L = 1.54$ M; (5) $C_M = 2.35\times10^{-2}$ M; $C_L = 1.34\times10^1$ M.

each species, present in the five samples. In other words, Table 1 represents a submatrix of the complete concentration matrix C. The powder absorption spectra of $UO_2(NO_3)_2\cdot6H_2O$ and $CsUO_2(NO_3)_3$ were used as an extra input to the deconvolution program.

In Fig. 3 the single component spectra of UO_2^{2+}, $UO_2NO_3^+$, $UO_2(NO_3)_2$ and $UO_2(NO_3)_3^-$ are shown, which are obtained from the deconvoluted mixed species spectra. The molar absorptivities of HNO_3 and NO_3^- were not plotted, because these species do not absorb in the region from 20 000 to 28 000 cm^{-1}. The values of ε_{ij} were also calculated as being zero.

The single component spectra are compared with literature data. The positions of the maxima $\nu_E + n_S\nu_S$ (cm^{-1}), the vibronic intervals $\Delta\nu_S$ (cm^{-1}) and the molar absorptivities ε (l mol^{-1} cm^{-1}) of the calculated spectra of UO_2^{2+}, $UO_2(NO_3)_2$ and $UO_2(NO_3)_3^-$ are given in Table 2. For the spectrum of UO_2^{2+}, the data for the uncomplexed hydrated ion is taken as a reference [2,36], whilst the calculated spectra $UO_2(NO_3)_2$ and $UO_2(NO_3)_3^-$ are compared with the spectra of the relevant compounds in the solid state [5].

In the absorption spectrum of $UO_2NO_3^+$, the different electronic transitions cannot be distinguished as well as the typical vibronic progressions, because of the low symmetry, which can be expressed by the C_s symmetry [5]. This property is also observed in the calculated spectrum.

5. Conclusions

A routine was written to obtain single-component spectra by evaluating a mixed species system. Preliminary results on a uranyl nitrate system in aqueous medium are promising, but the problem of the uncertainties of the stability constants remains. This preliminary study can be seen as a method for optimising the stepwise formation constants. It is our goal to expand this study to other complex systems, also in organic solvents.

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Table 1
Submatrix of the complete calculated concentration matrix C^a

	$[UO_2^{2+}]$ (M)	$[UO_2NO_3^+]$ (ML)	$[UO_2(NO_3)_2]$ (ML_2)	$[UO_2(NO_3)_3^-]$ (ML_3)	$[NO_3^-]$ (L)
(1)	1.79×10^{-2}	2.17×10^{-3}	5.28×10^{-4}	1.16×10^{-4}	2.43×10^{-1}
(2)	9.15×10^{-3}	4.76×10^{-3}	4.96×10^{-3}	4.64×10^{-3}	1.04
(3)	6.61×10^{-3}	3.69×10^{-3}	4.12×10^{-3}	4.14×10^{-3}	1.12
(4)	3.96×10^{-3}	2.99×10^{-3}	4.53×10^{-3}	6.16×10^{-3}	1.51
(5)	2.04×10^{-5}	1.36×10^{-4}	1.80×10^{-3}	2.16×10^{-2}	13.3

[a] All concentrations in M. (1) $C_M=2.07\times10^{-2}$ M; $C_L=2.47\times10^{-1}$ M; (2) $C_M=2.35\times10^{-2}$ M; $C_L=1.07$ M; (3) $C_M=1.86\times10^{-2}$ M; $C_L=1.14$ M; (4) $C_M=1.76\times10^{-2}$ M; $C_L=1.54$ M; (5) $C_M=2.35\times10^{-2}$ M; $C_L=1.34\times10^1$ M.

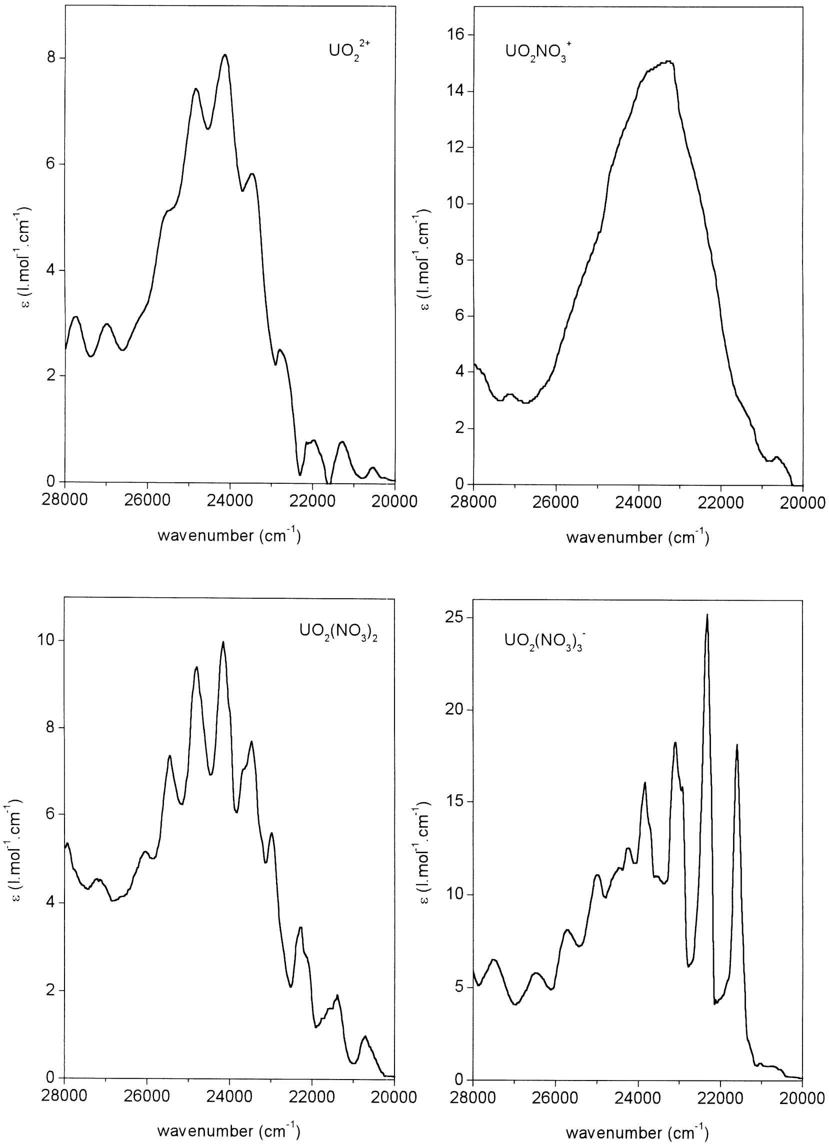

Fig. 3. Single-component spectra of UO_2^{2+}, $UO_2NO_3^+$, $UO_2(NO_3)_2$ and $UO_2(NO_3)_3$. Results after deconvolution of the mixed species spectra. Note that each figure has been scaled differently.

Table 2
Analysis of the single-component spectra of UO_2^{2+}, $UO_2(NO_3)_2$ and $UO_2(NO_3)_3^-$ and the comparison with literature data[a]

$UO_{2\ \mathrm{calc.}}^{2+}$			UO_2^{2+} [2,36]			$UO_2(NO_3)_{2\ \mathrm{calc.}}$			$UO_2(NO_3)_2 \cdot 6H_2O$ [5]			$UO_2(NO_3)_{3\ \mathrm{calc.}}^-$			$CsUO_2(NO_3)_3$ [5]		
$\nu_E + n_S \nu_S$	$\Delta\nu_S$	ε	$\nu_E + n_S \nu_S$	$\Delta\nu_S$	ε	$\nu_E + n_S \nu_S$	$\Delta\nu_S$	ε	$\nu_E + n_S \nu_S$	$\Delta\nu_S$	ε	$\nu_E + n_S \nu_S$	$\Delta\nu_S$	ε	$\nu_E + n_S \nu_S$	$\Delta\nu_S$	ε
20 534	–	0.3	20 619	–	0.3	20 712	–	1.0	20 600	–	1.6	20 773	–	0.8	21 075	–	1.3
21 286	752	0.8	21 415	796	0.8	21 395	683	1.9	21 310	710	2.5	21 607	34	18	21 675	810	20
21 978	692	1.4	22 173	753	1.6	22 272	877	3.5	22 030	720	3	22 331	724	25	22 420	745	26.5
22 810	832	2.5	22 886	713	3.3	22 988	716	5.6	22 705	675	6	23 105	774	18	23 170	750	20
23 485	675	5.8	23 530	644	5.9	23 474	486	7.7	23 415	710	8.5	23 844	739	16	23 910	740	16
24 143	658	8.1	24 219	689	7.8	24 154	680	10	24 130	715	11.5	24 510	666	11.4	24 640	730	12.5
2439	696	7.4	24 878	659	7.0	24 802	648	9.4	24 830	700	11	23 585	480	11	23 530	360	12
25 562	723	5.1	25 580	702	4.9	25 458	656	7.4	25 550	720	9.3	24 237	652	12.5	24 310	780	13.5
2628	726	3.0	26 316	736	2.8	26 042	584	5.2	26 245	695	7.3	24 987	750	11.1	25 050	740	12.5
26 998	710	3.0	27 119	803	2.8	26 638	596	4.2	26 955	710	6	25 720	733	9.77	25 820	770	10
27 747	749	3.1	27 882	763	3.1	27 218	580	4.5	27 260	305	6.2	26 511	791	5.8	26 540	720	7.5
						27 949	731	5.3	28 050	790	7	27 533	1022	6.5	27 525	985	7.5
						–	–	–	28 440	790	7	28 265	732	8.7	28 310	785	8.5

[a] Units: $\nu_E + n_S \nu_S$ (cm^{-1}), $\Delta\nu_S$ (cm^{-1}), and ε (l mol^{-1} cm^{-1}).

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